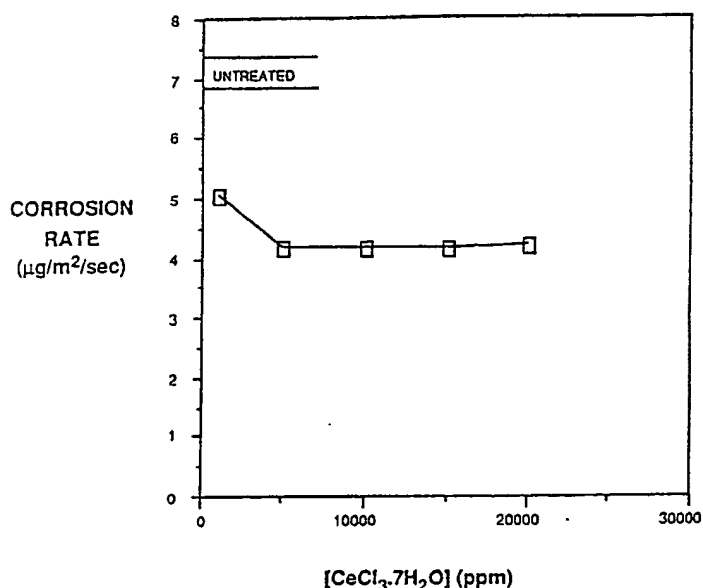




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(54) Title: A METHOD OF FORMING A CORROSION RESISTANT COATINGEFFECT OF CERIOUS CHLORIDE
CONCENTRATION ON CORROSION RATE**(57) Abstract**

A method forming a cerium based coating onto the surface of a metal is characterised by forming an acidic solution having a pH below that at which cerium precipitates, oxidising cerium cations from the +3 to the +4 valency state and immersing the metal in the acidic solution thereby to increase the pH sufficiently to cause cerium to precipitate on the metal.

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A METHOD OF FORMING A CORROSION RESISTANT COATING

The present invention relates to a method of forming coatings on metal surfaces to inhibit corrosion.

Corrosion is an electrochemical process generally consisting of two or more partial reactions. At anodic sites on the metal surface dissolution occurs, which for aluminium is written $\text{Al} \longrightarrow \text{Al}^{3+} + 3\text{e}^-$. At cathodic sites, which may be copper or iron rich micro-constituents, cathodic reactions such as the reduction of oxygen ($\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-$) and the

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evolution of hydrogen $2H^+ + 2e^- \longrightarrow H_2$ occur. Inhibition of corrosion can be achieved if any of these reactions can be stopped or the rates at which they proceed reduced.

For many years, chromates have been the accepted inhibitors of corrosion of aluminium alloys in aqueous environments. In the aircraft industry chromates are employed in paint films and sealants. Chromates are classified as anodic inhibitors because they prevent metal dissolution by forming a stable passive film on the metal surface.

Zinc salts have also been used to inhibit corrosion. Inhibition by zinc cations results from the deposition of insoluble zinc hydroxide at cathodic sites promoting reduced rates of cathodic reaction. Thus, zinc is classified as a cathodic inhibitor. In practice, it is frequently used as zinc phosphate.

The recently recognised toxicity of chromates together with the adverse effects of phosphates on natural waterways has led to interest in the use of more environmentally acceptable chemicals for corrosion inhibition.

It has been reported in an article by B.R.W. Hinton, D.R. Arnott, L. Wilson and others entitled "The Inhibition of Aluminium Alloy Corrosion by Rare Earth Metal Cations" published in Corrosion Australia June 1985 that additions of cerous cations to sodium chloride solution significantly reduce the rate of corrosion of 7075 aluminium alloy. It was found that the cerous cations act as a cathodic inhibitor.

The corrosion resistance was attributed to the formation of a complex hydrated cerium oxide film on the

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aluminium alloy. The research suggested that the cerium oxide film, if applied as a coating to 7075 aluminium alloy, could offer protection against corrosion in chloride containing environments.

Subsequent research showed that three methods
5 of treatment could cause the formation of a coating which contained cerium oxide. The findings of the research was reported in an article by B.R.W. Hinton, D.R. Arnott and N.E. Ryan entitled "Cerium Conversion Coatings for the Corrosion Protection of Aluminium"
10 published in Vol. 9 No. 3 (1986) of Metals Forum. The methods of treatment disclosed in the article are (a) open circuit exposure to cerous chloride solution, (b) cathodic treatment in aqueous cerous chloride solution, or (c) cathodic treatment in cerous nitrate dissolved in
15 butoxyethanol.

However, it was found that the coatings prepared at open circuit potential are not a viable option from the practical viewpoint because they take over 100 hours to prepare. Furthermore, it was found
20 that, whilst coatings can be prepared cathodically in aqueous solutions in as little as 0.5 hours, in many instances, the coatings lack durability because of blistering on the surface and thus have limited practical applications. Furthermore, whilst it was
25 found that coatings formed by cathodic treatment in cerous nitrate dissolved in butoxyethanol could be formed in as little as 150 seconds, in many instances, the coatings are subject to cracking and thus have limited practical applications. A more significant
30 problem for both cathodic treatments is that the equipment required and the procedure involved in the cathodic treatments are generally inconvenient from a practical viewpoint.

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It is an object of the present invention to provide a method of forming a cerium based coating onto a metal surface which alleviates the disadvantages of the prior art methods described above.

5 In accordance with the present invention there is provided a method of forming a coating containing cerium on the surface of a metal, comprising:

- (a) forming an aqueous acidic solution containing cerium cations,
- 10 (b) oxidising the cerium cations to the +4 valency state, and
- (c) contacting the acidic solution with the metal surface thereby to cause the evolution of gaseous hydrogen in the region of the metal surface with the
15 result that the pH of the acidic solution increases in the region of the metal surface to a value in excess of that required to precipitate the cerium
20 in the +4 valency state thereby to cause cerium to precipitate onto the metal surface uniformly over the whole of the metal surface.

It is preferred that the method comprises the
25 use of hydrogen peroxide as the oxidising agent. In this regard, the preferred method comprises:

- (a) mixing a cerium salt and hydrogen peroxide to form an aqueous acidic solution in which the cerium cations are
30 substantially oxidised to the +4 valency state,

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- 5 (b) contacting the acidic solution with the metal surface thereby to cause evolution of gaseous hydrogen in the region of the metal surface with the result that the pH of the acidic solution increases in the region of the metal surface to cause precipitation of ceric hydro peroxide onto the metal surface uniformly over the whole of the metal surface in
10 contact with the solution, and
- (c) drying the metal surface to convert the ceric hydro peroxide to hydrated cerium oxide.

15 It is preferred that the metal is any one of aluminium, steel, zinc, cadmium and magnesium.

It is preferred that the cerium salt is cerium chloride.

20 It is preferred that the pH of the acidic solution is less than 3.0 prior to contact with the metal surface.

It is preferred that the pH of the acid solution is above 3.0 in the region of the metal surface after contact with the metal surface.

25 The quality of the coating is dependent on a number of factors such as the concentration of cerium cations in the acidic solution and the contact time of the acidic solution with the metal surface. It is preferred that the concentration of the cerium cations is between 5000 and 15000 parts per million (ppm) and

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the contact time is less than 60 minutes. It is particularly preferred that the concentration of the cerium cations is 10000 ppm and the contact time is 7 minutes.

5 A number of test specimens were prepared by forming coatings on samples of 7075 aluminium alloy plate (Al, 5.6% Zn, 2.5% Mg, 1.6% Cu, 0.3% Cr). Each test specimen was formed by mixing together cerous chloride and hydrogen peroxide to form an aqueous acidic
10 solution and then immersing samples of 7075 aluminium alloy plate in the acidic solution to form a coating thereon. The effect of the following variables on corrosion rate of the test specimens was investigated:

- (a) pH of the acidic solution,
- 15 (b) concentration of hydrogen peroxide;
- (c) concentration of cerous chloride;
- (d) temperature of the acidic solution during immersion of samples of 7075 aluminium alloy plate; and
- 20 (e) time of immersion of samples 7075 aluminium alloy plate.

The results of the investigations are shown in the graphs in Figures 1 to 5.

25 The graph in Figure 1 illustrates the effect of the concentration of cerous chloride in the acidic solution on the corrosion rate of a series of test specimens prepared under the following conditions:

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- (a) pH: 2.7;
- (b) concentration of H_2O_2 : 5%;
- (c) temperature of immersion: 50°C ; and
- (d) time of immersion: 10 minutes.

5 The graph indicates that only a small
concentration of cerous chloride in the acidic solution
was required to form corrosion-resistant coatings on the
samples of 7075 aluminium alloy plate. Specifically, a
corrosion rate of $5 \mu\text{g}/\text{m}^2/\text{sec}$ was recorded with a test
10 specimen prepared in an acidic solution having only 100
ppm cerous chloride. This corrosion rate compares with
a corrosion rate of $7 \mu\text{g}/\text{m}^2/\text{sec}$ recorded with a sample
of untreated 7075 aluminium alloy plate.

15 In this regard, the graph in figure 1 also
confirms the effectiveness of the use of cerium to form
corrosion-resistant coatings. Specifically, the graph
indicates that corrosion rates of only $4.2 \mu\text{g}/\text{m}^2/\text{sec}$
were recorded with test specimens prepared in acidic
solutions containing between 5000 and 20,000 ppm cerous
20 chloride (cf corrosion rate of $7 \mu\text{g}/\text{m}^2/\text{sec}$ for untreated
samples of 7075 aluminium alloy plate).

25 The graph in Figure 2 illustrates the effect of
the concentration of hydrogen peroxide in the acidic
solution on the corrosion rate of a series of test
specimens prepared under the following conditions:

- (a) concentration of $\text{CeCl}_3 \cdot (7\text{H}_2\text{O})$: 10,00 ppm;
- (b) pH: 2.7;

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(c) temperature of immersion: 50°C; and

(d) time of immersion: 10 minutes.

The graph indicates that the concentration of hydrogen peroxide in the acidic solution had a significant effect on the corrosion-resistant characteristics of the coatings formed on the samples of 7075 aluminium alloy plate. This is reflected by the fact that a relatively high corrosion rate of 5.5 $\mu\text{g}/\text{m}^2/\text{sec}$ was recorded with a test specimen prepared in an acidic solution containing 1% hydrogen peroxide, whereas a corrosion rate of only 3.6 $\mu\text{g}/\text{m}^2/\text{sec}$ was recorded with a test specimen prepared in an acidic solution containing 3% hydrogen peroxide.

The graph in figure 3 illustrates the effect of the pH of the acidic solution on the corrosion rate of a series of test specimens prepared under the following conditions.:

(a) concentration of $\text{CeCl}_3 \cdot (7\text{H}_2\text{O})$: 10,000 ppm;

(b) concentration of H_2O_2 : 5%;

(c) temperature of immersion: 50°C; and

(d) time of immersion: 10 minutes.

The graph indicates that the pH of the acidic solution had a significant effect on the corrosion-resistant characteristics of coatings formed on the samples of 7075 aluminium alloy plate. Specifically, relatively low corrosion rates of approximately 4 $\mu\text{g}/\text{m}^2/\text{sec}$ were recorded with test specimens prepared in acidic solutions of pH between 2

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and 3, whereas a corrosion rate of $6.5 \mu\text{g}/\text{m}^2/\text{sec}$ was recorded with a test specimen prepared in an acidic solution of pH 1.

The profile of the graph in Figure 3 indicates an optimum range of values of pH centred on 2.5. It is thought that the progressive increase in corrosion rate as the pH decreased from 2.5 was due to the pH being increasingly too low for the subsequent increase in pH following contact with the samples of 7075 aluminium alloy plate to reach a threshold pH at which cerium precipitates. Moreover, whilst not clearly shown in the graph, it is expected that the corrosion rate would progressively increase as the pH increased from 2.5, and it is thought this trend would be due to cerium precipitating in the bulk of the acidic solution rate than as a coating on the samples of 7075 aluminium alloy plate.

The graphs in Figures 4 and 5 respectively illustrate the effect of immersion time and immersion temperature on the corrosion rate of a series of test specimens prepared under the set conditions for the pH of the acidic solution and concentrations of H_2O_2 and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ described above. The graph in Figure 4 indicates that an immersion time of only 3 minutes was necessary to form a corrosion-resistant coating on a sample of 7075 aluminium alloy plate, and the graph in Figure 5 indicates that the temperature of the acidic solution did not affect significantly the corrosion-resistant characteristics of the coatings formed on the samples of 7075 aluminium alloy plate.

A series of experiments was carried out to investigate the adhesion of an epoxy primer/polyurethane paint film to coatings formed from cerium. The experiments comprised forming a paint film on the test specimens and then gluing a block having an upstanding shaft onto the paint film. The block was then rotated

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about the axis of the shaft while the plate was held stationary. The torque at failure was determined to provide a measure of the adhesion strength of the paint film to the coatings.

5 In two experiments carried out on samples of chromated aluminium alloy plate the measured values of torque at failure were 25.9 and 26.9 MNm^{-2} . In three experiments carried out on samples of aluminium alloy plate having a coating formed from cerium the measured
10 values of torque at failure were 31.3, 31.3 and 30.9 MNm^{-2} . Moreover, in the case of the first two experiments the failure occurred at the interface of the block and the paint film and not at the interface of paint film and the coatings. Thus, the experiments
15 indicated that the coatings had good adhesion properties for paint film.

 In a further series of investigations, test specimens similar to those described in the foregoing were prepared. The only change in the procedure for
20 preparing the test specimens was the addition of brighteners to the acidic solution. Typically, the brighteners included pearl glue, dextrose, glucose and starch. It was found that there was a further lowering of the corrosion rates of the test specimens.
25 Specifically, corrosion rates as low as $1.5 \mu\text{g}/\text{m}^2/\text{sec}$ were recorded.

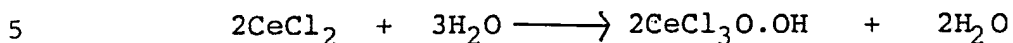
 In a further series of investigations, test specimens were prepared by forming coatings on zinc plate rather than 7075 aluminium plate. It was found
30 that the rate of corrosion of the test specimens was up to 8 times less than the rate of corrosion of untreated zinc plate.

 It is believed that the mechanism for the formation of the coatings of the aluminium alloy plate

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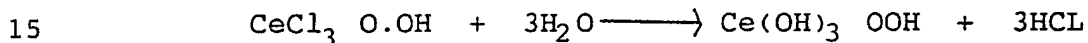
and the zinc plate is as follows:

1. Cerous chloride and hydrogen peroxide react to form ceric chloro peroxide in accordance with the following reaction:



2. The acidic solution thus formed has a pH approximately 2, and when the metal contacts the solution the surface layers of the metal are attacked and hydrogen is evolved. The evolution of hydrogen
10 results in an increase in the pH at the metal surface.

3. The increase in the pH results in the precipitation of ceric hydro peroxide which deposits as a thin coating on the metal surface in accordance with the following reaction:



4. Drying of the coating converts the ceric hydro peroxide to hydrated cerium oxide.

The above preferred method of forming a cerium cation coating has a number of advantages over the known
20 methods. One of the advantages is that the method is not dependent on applying a cathodic potential to form a coating in a reasonable time. Another advantage is that the method results in coatings that are uniform, have good corrosion properties and paint film adhesion
25 properties.

Many modifications may be made without departing from the spirit and scope of the present invention. In this regard, whilst the invention has been described in relation to the use of cerous chloride

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as the source of cerium cations, it can readily be appreciated that the invention is equally applicable to any source of cerium cations, such as mixtures of rare earth chlorides which include cerous chloride, cerous
5 sulphate, mischmetall chloride, cerous perchlorate, cerium acetyl acetonate, and cerous nitrate.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of forming a surface coating containing cerium on the surface of a metal comprising:

(a) forming an aqueous acidic solution containing cerium cations,

(b) oxidising the cerium cations to the +4 valency state, and

(c) contacting the acidic solution with the metal surface thereby to cause the evolution of gaseous hydrogen in the region of the metal surface with the result that the pH of the acidic solution increases in the region of the metal surface to a value in excess of that required to precipitate the cerium in the +4 valency state thereby to cause cerium to precipitate onto the metal surface uniformly over the whole of the metal surface.

2. The method defined in claim 1, wherein the cerium cations are oxidised to the +4 valency state by mixing hydrogen peroxide after or during the preparation of the aqueous acidic solution.

3. The method defined in claim 1 or claim 2, further comprises drying the metal surface to convert the ceric hydro peroxide to hydrated cerium oxide.

4. The method defined in any one of the preceding claims, wherein the metal is any one of aluminium, steel, zinc, cadmium and magnesium.

5. The method defined in any one of the preceding claims, wherein the source of cerium cations is cerium chloride.

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6. The method defined in any one of the preceding claims, wherein the pH of the acidic solution is less than 3 prior to contact with the metal surface.

7. The method defined in claim 6, wherein the pH of the acidic solution is greater than 1 prior to contact with the metal surface.

8. The method defined in any one of the preceding claims, wherein the pH of the acidic solution is above 3 in the region of the metal surface after contact with the metal surface.

9. The method defined in any one of the preceding claims, further comprises adding brighteners to the acidic solution prior to or during immersion of the metal surface.

10. A coated metal surface formed in accordance with the method defined in any one of the preceding claims.

EFFECT OF CERIOUS CHLORIDE CONCENTRATION ON CORROSION RATE

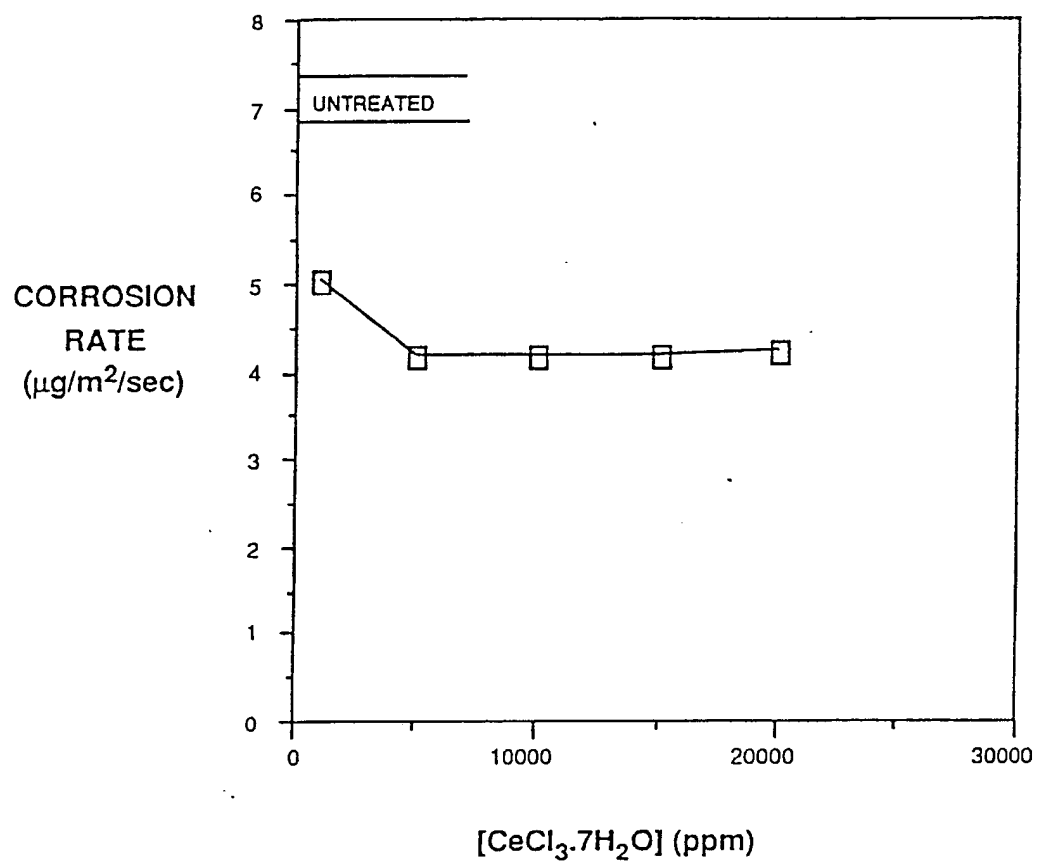


FIGURE 1

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EFFECT OF HYDROGEN PEROXIDE CONCENTRATION ON CORROSION RATE

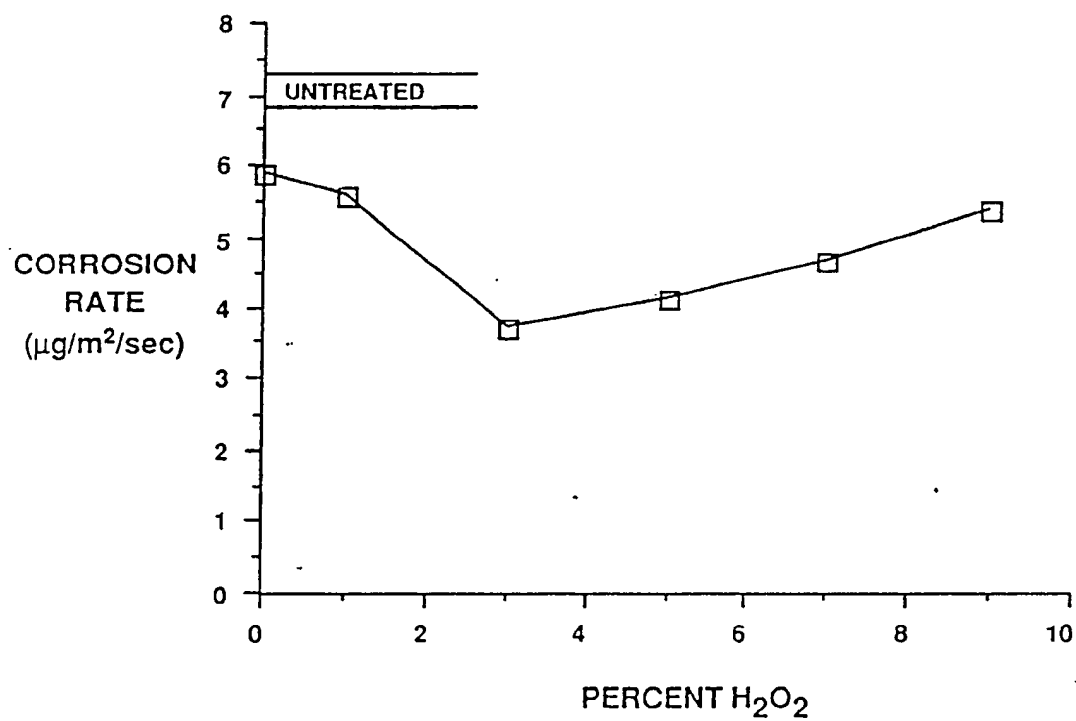


FIGURE 2

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EFFECT OF SOLUTION pH ON CORROSION RATE

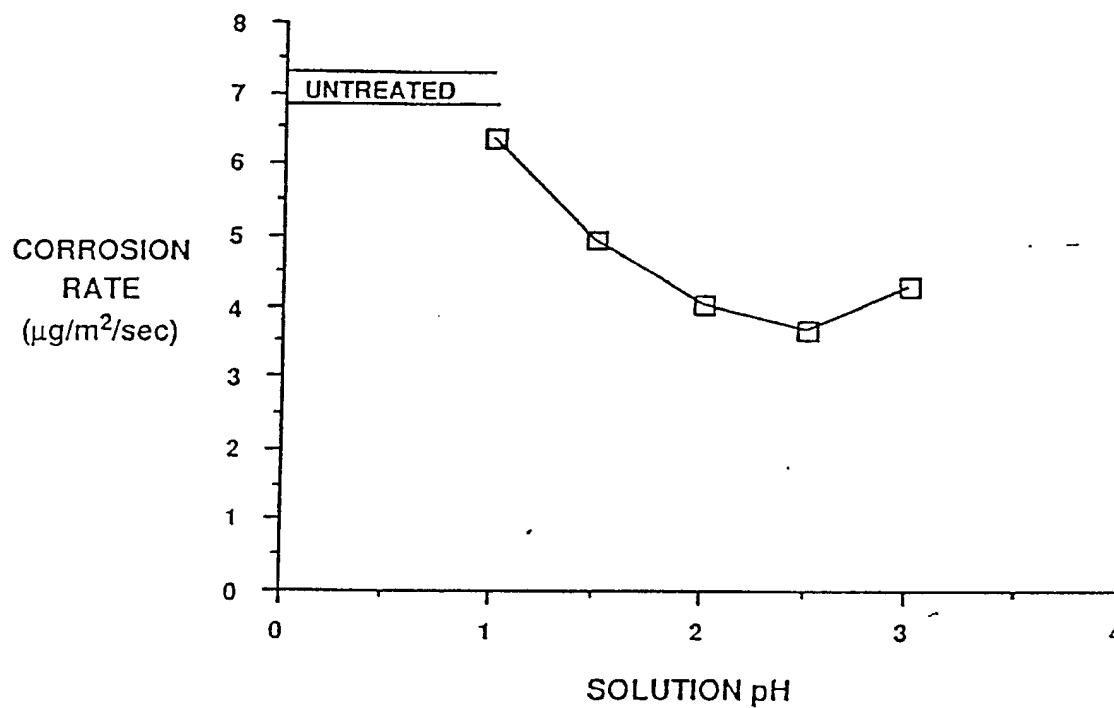
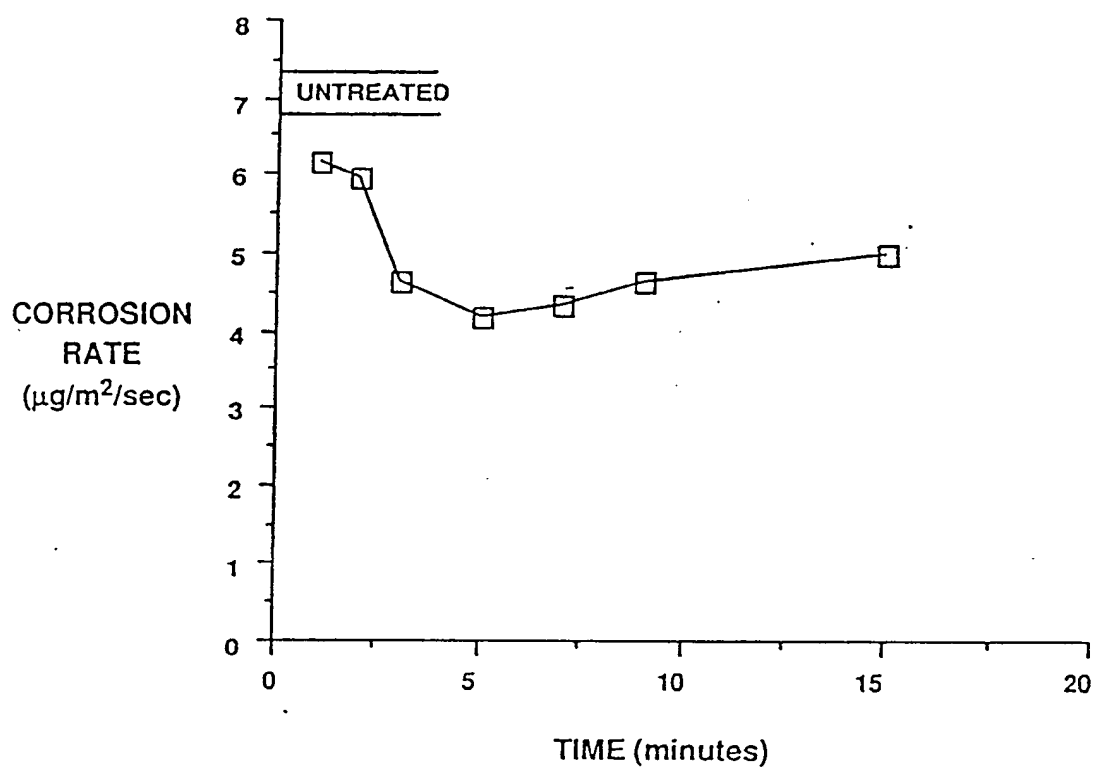


FIGURE 3

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EFFECT OF IMMERSION TIME ON
CORROSION RATEFIGURE 4

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EFFECT OF IMMERSION TEMPERATURE ON CORROSION RATE

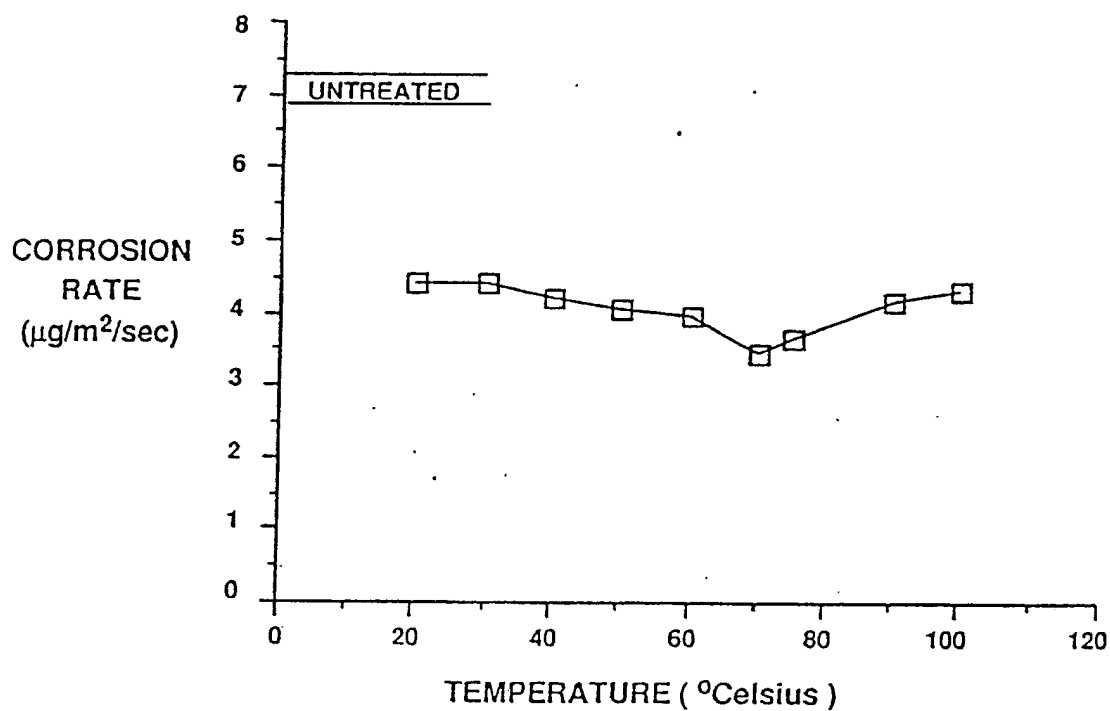


FIGURE 5

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INTERNATIONAL SEARCH REPORT

International Application No PCT/AU 88/00060

I. CLASSIFICATION OF SUBJECT MATTER (1) several classification symbols apply. Indicate all: 2		
According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. 4 C23C 22/48, 22/50, 22/53, 22/56, C23F 11/18		
II. FIELDS SEARCHED		
Minimum Documentation Searched 7		
Classification System	Classification Symbols	
IPC	C23C 22/48, 22/50, 22/53, 22/56, C23F 11/18	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8		
AU : IPC as above, C23F 7/04		
III. DOCUMENTS CONSIDERED TO BE RELEVANT 9		
Category 10	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
A	AU,A, 35661/84 (DUGGAN) 23 May 1985 (23.05.85) See page 5 last paragraph	(1)
A	AU,B, 32947/84 (565065) (THE BRITISH PETROLEUM COMPANY p.l.c.) 3 September 1987 (03.09.87) See page 2 paragraphs 3 and 4	(1)
A	US,A, 4297246 (CAIRNS et al) 27 October 1981 (27.10.81) See Example 1, pages 5 and 6	(1)
A	GB,A, 1418957 (LONG et al) 24 December 1975 (24.12.75) See page 2 lines 34-43	(1)
A	US,A, 4328285 (SIEMERS et al) 4 May 1982 (04.05.82)	(1)
A	Chemical Abstracts, Volume 106, No.8, issued 1987, February 23 (Columbus, Ohio, USA), B.R.W. Hinton et al, 'Cerium Conversion Coatings for the Corrosion Protection of Aluminium', see page 256, Column 1, the abstract No. 54262n, Mater. Forum 1986, 9(3), 162-75 (Eng.)	(1)
(continued)		
* Special categories of cited documents: 16 - "A" document defining the general state of the art which is not considered to be of particular relevance - "E" earlier document but published on or after the international filing date - "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) - "O" document referring to an oral disclosure, use, exhibition or other means - "P" document published prior to the international filing date but later than the priority date claimed - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention - "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step - "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu- ments, such combination being obvious to a person skilled in the art. - "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 29 April 1988 (29.04.88)		Date of Mailing of this International Search Report (05.05.88) 3 MAY 1988
International Searching Authority Australian Patent Office		Signature of Authorized Officer R.A. MELVIN

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

- | | | |
|---|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| A | Chemical Abstracts, Volume 103, No.12, issued 1985 September 9, D.R. Arnott et al, 'Auger and XPS Studies of Cerium Corrosion Inhibition on 7075 Aluminium Alloy', see page 237, Column 2, the abstract No. 91568a, Appl. Surf. Sci. 1985, 22-23(1), 236-51 (Eng.) | (1) |
| A | Chemical Abstracts, Volume 96, No.26, issued 1982, 28 June, M.J. Bennett et al, 'Influence of Thermal and Mechanical Stresses on the Improvement by Ceramic Protective Surface Coatings of the Oxidation Behaviour of a 20%/25% Nickel/Niobium Stabilised Stainless Steel', see page 224, Column 2, the abstract No. 221202b, Met. Corros. Proc.: Int. Congr. Met. Corros./, 8th 1981, 2, 1026-31 (Eng.) | (1) |

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim numbers because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 88/00060

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members			
AU 35661/84	CA 1228266	DE 3442250	GB 2150158		
	US 4658761				
AU 32947/84	BR 8404652	DK 4391/84	EP 136860		
	JP 60086287				
	ZA 8407192	NO 843658	NZ 209554		
US 4297246	CA 1118301	FR 2416743	FR 2416867		
	GB 2023453	GB 2087250	GB 2087632		
	NL 7810883	SE 7905691	SE 8201621		
	US 4231893	US 4427721	WO 7900247		
	WO 7900248	GB 1603794	NL 7810884		
	GB 1600871				
GB 1418957	DE 2319673	FR 2184003	JP 49061033		
US 4328285	DE 3127232	FR 2486966	GB 2080147		
	IL 62740	IT 1137607	JP 57032374		
	NL 8103185				

END OF ANNEX